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NATIONAL TECHNICAL
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PERSISTENCE OF MONO-CHLOROPHENOLS IN POLLUTED RIVER WATER AND SEWAGE DILUTIONS*

The factors which determine the persistence of phenol and the cresols in surface waters have already been studied and reported (1). Briefly, it was found that phenol and the cresols are dissipated in surface waters by biological oxidation. The persistence of these materials appears to be governed by those factors which determine biological oxidation rates.

Further studies of the persistence of individual materials appeared to be very much needed. There can be no better way to improve the overall knowledge of self purification factors than to study the persistence of individual compounds. Ortho and para-chlorophenols were chosen for early study because adequate analytical methods, sensitive to a few parts per billion of these materials already were available (2).

However, as these chlorinated phenols are likely to be of infrequent occurrence in surface waters they have been investigated on a limited scale at 20°C. Enough work was undertaken to give a fair indication of the behavior that might be expected from these organic compounds.

Analytical Techniques

The analytical technique used in the study has been a modification of the Gibbs method as previously described (2). Para-chlorophenol

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does not give a very intense reaction using this technique. Apparently this is because the reagent first has to dechlorinate the para-chlorophenol and react with the resultant phenol. The color is produced more slowly and the final intensity is lower than would be obtained with an equivalent amount of phenol. In the case of ortho-chlorophenol, the reaction appears to be relatively rapid. For this chemical, the reaction has a linear range for concentrations which appear to extend well beyond 100 p.p.b.

The wave lengths used for quantitative measurements on a Beckman DU Spectrophotometer were 670 millimicrons for para-chlorophenol and 690 millimicrons for ortho-chlorophenol.

Some attempts were made to use ultra-violet absorption measurements rather than the Gibbs reaction as a basis for the analytical measurements. However, the ultra-violet observations appeared to be less satisfactory than the procedure in the visual range. One of the principal difficulties was the high background ultra-violet absorption noted in the distillate from polluted river samples. In attempting analytical examination of polluted river samples, the absorption due to chlorinated phenol appeared superimposed upon that due to other materials distilled from acid solutions of the river water. Furthermore, the absorption of ultra-violet radiation caused by other materials in the polluted water was not necessarily constant for the duration of an experiment. It appeared, therefore, that measurement of the absorption by the more specific colors developed by the Gibbs reagent was the more satisfactory method of testing for the chlorophenols in question.

Persistence Data

In the first persistence experiments, ortho and para-chlorophenol were added to 1 per cent dilutions of sewage in standard B.O.D. dilution water. Two series of observations for periods up to 25 days at 20°C. were made on each of these chlorophenols. The data on these studies are shown in Table 1. In three of these series of observations, no dissimilation of the chlorinated phenol appears to have taken place, at least not within the accuracy of the analytical measurements. In the fourth case, apparently para-chlorophenol was slightly attacked in one sewage dilution in 23 days.

The preliminary experiments led to the belief that these chlorophenols were relatively immune to biochemical attack. Further investigation showed that such was not the case. The next experiments consisted of adding 1 p.p.m. of ortho and para-chlorophenol to relatively polluted river waters. The results are shown in Table 2. It may be seen that these materials were attacked much more rapidly when added to the river water than when added to the sewage dilution. This more rapid attack is probably due to the presence of microorganisms in the river water capable of destroying ortho or para-chlorophenol.

While these chlorophenols were removed much more quickly from the river waters than from sewage dilutions, the overall persistence was very much greater than was found for phenol and the cresols under similar circumstances (1).

TABLE 1

PERSISTENCE OF PARA AND ORTHO-CHLOROPHENOLS IN B.O.D. DILUTION WATER CONTAINING 1 PER CENT DOMESTIC SEWAGE AT 20°C.

Chlorophenol Used	Residual Chlorophenol p.p.b.			
	para-chlorophenol		ortho-chlorophenol	
Experiment Number	1	2	3	4
Days Stored				
0	1060	-	1130	-
1		960		1120
3	1300 ?		1110	
8		980		990
10	980		810	
15		880		1000
17	920		1020	
23		650		960
25	1000		930	

TABLE 2

PERSISTENCE OF MONO-CHLOROPHENOLS ADDED TO SEVERAL SURFACE WATERS AT 20°C.

Days Stored	Residual Mono-chlorophenols, p.p.b.			
	Great Miami River Water		Little Miami River Water	
	o-chlorophenol	p-chlorophenol	o-chlorophenol	p-chlorophenol
0	980	1,000	890	1,000
6	810	980	870	1,000
13	790	80	480	0
15	760	0	0	0
23	710	0	0	0
36	0	0	0	0

Next, the effect of seeding was investigated. Parallel studies were made of the persistence of ortho-chlorophenol added to the two river waters, with and without seeding. In one case, the ortho-chlorophenol was simply added to the river water. Concurrently, another portion was prepared in which the same concentration of the ortho-chlorophenol was introduced along with a small amount of seed. The seed used consisted simply of some river water from a prior persistence experiment, and presumably introduced a number of organisms which attacked the chemical. The results of these experiments are given in Table 3.

The addition of the seed reduced the persistence of the ortho-chlorophenol in the case of one of the river waters in this series of experiments. However, the unseeded experiments of Table 2 show about the same overall persistence of ortho-chlorophenol as is shown in the seeded samples of Table 3. This indicates that while the seed is important, it is by no means the only factor.

Discussion of the Data

Throughout this paper, it has been assumed that biochemical action is responsible for the dissipation of the chlorophenols studied. There are a number of reasons for accepting this premise.

(a) Previously [1] it was demonstrated that phenol is quite stable in sterile solutions, but is rapidly attacked in the presence of a suitable microflora.

TABLE 3

PERSISTENCE OF 1,000 P.P.B. ADDITIONS OF ORTHO-CHLOROPHENOLS IN SURFACE WATERS

Days Stored	Residual Ortho-chlorophenol, p.p.b.			
	Great Miami River Water		Little Miami River Water	
	Unseeded	Seeded*	Unseeded	Seeded*
0	1,000	1,000	1,000	1,000
1	-	800	930	730
5	900	600	890	690
6	700	530	550	620
8	650	300	570	200
13	610	10	20	80
15	320	-	-	0
19	30	-	-	-

(*) Seed consisted of 1/2 ml. per liter of ortho-chlorophenol using river water

(b) The data definitely point toward biochemical dissimilation as the mechanism whereby the chlorinated phenols are dissipated.

(c) No other mechanism can be postulated which is consistent with all the observations.

The chemical nature of the mono-chlorophenols suggests that the number of species of microorganisms which will attack these materials is highly limited. The data presented are definitely in accord with this premise. It is interesting to note that two samples of sewage failed to yield organisms capable of attacking these materials within a reasonable period of time. On the other hand, both river waters apparently contained such a seed.

The general implications of the study are plain:

(1) Ortho or para-chlorophenol may be attacked by biological agencies in a surface water.

(2) The attack on such material, even under favorable conditions, will proceed at a slow rate.

(3) Ortho or para-chlorophenol may persist for long periods if discharged occasionally into a relatively pure stream. However, it would appear likely that a bacterial flora capable of destroying these chlorophenols would soon be established if the wastes are discharged regularly.

Summary and Conclusions

It has been shown that low concentrations (1,000 p.p.b.) of ortho and para-chlorophenol, when added to the ordinary dilutions of domestic sewage, were not always removed in periods of 20 to 30 days at 20°C. Similar concentrations of these mono-chlorophenols were removed at this temperature during similar periods of storage when added to polluted surface waters. These observations on the conditions required for the dissipation of mono-chlorophenols in surface waters and sewage dilutions along with previous observations on the similar dissipation of cresols and phenol indicate that biochemical dissimilation is responsible for the removal of these materials. The study has also shown that the removal of these mono-chlorophenols requires the presence of a specialized microflora and in general proceeds at lower rates than the similar removal of the cresols and phenol.

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Bibliography

(1) Ettinger, M. B., and Ruchhoft, C. C.
"Removal of Phenol and Cresols from Natural Waters".
Ind. and Eng. Chem., 41, 1422-7 (1949).

(2) Ettinger, M. B., and Ruchhoft, C. C.
"Determination of Phenol and Structurally Related
Compounds by the Gibbs Method". Anal. Chem., 20,
1191-6 (1948).